

Development of a 3d current collector for the positive electrode in lithium-ion batteries

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Abstract So far, expanded metals or metal foils have been used as current collectors for the positive electrode in state of the art lithium-ion batteries (LIBs). In this work, a new 3D current collector for the positive electrode of LIBs was investigated. Non-woven polymer was metallized with Al by physical vapour deposition (PVD). To prove its feasible application as a current collector in LIBs, LiCoO₂ (LCO) composite electrodes were fabricated and compared to common LCO composite electrodes coated on “state of the art” aluminium foil. All cathodes were characterised by scanning electron microscopy, as well as electrochemical methods, and the results were compared. In combination with the main advantages of 3D current collectors such as improved mechanical stability and possibility of higher mass loadings, the 3D structure of the non-woven polymer increases the contact surface by five times compared to conventional current collector foils, reducing the assignment of Al significantly.

Keywords Lithium-ion batteries · 3D current collector · Aluminium · Cathode

1 Introduction

Lithium-ion batteries (LIBs) are a fast-growing technology, used in portable electronic devices such as cell phones, digital cameras and laptops, due to their light weight and high power. Because of recent environmental concerns they are believed to be a major power source for future

electrical vehicle applications and energy storage. Therefore, it is necessary to reduce the volume and weight of LIBs for improvement of energy density (Wh L⁻¹) and specific energy (Wh kg⁻¹). There are conceivable possibilities such as the search for new cathode and anode materials with higher capacities or the refinement of the battery cell design to maximise energy density [1, 2]. A reduction of specific mass (g Wh⁻¹) of inactive components could be achieved by increasing mass loading of the electrode. However, the traditional architecture of battery electrode materials on flat metal current collectors does not allow higher mass loadings. This can be related to complexities such as delamination of electrode material from the flat metal foil, the difficulty of electrolyte penetration through a thick electrode or higher resistivity due to long electron paths to the current collector [3, 4]. These problems could be overcome with the implementation of 3D current collectors [5]. Examples are nano-tubes grown on metal foils [6], porous conductive textiles [4], carbon and metal foams [7, 8] or metal meshes [9]. Electrodes composed of the 3D porous textile conductor delineated by Hu et al. [4], fabricated by tipping polyester fibres into an ink of carbon nano-tubes dispersed in water, showed good electrochemical behaviour. The conductive textile was loaded with high masses of LiFePO₄ or Li₄Ti₅O₁₂ (LTO) and the cycling results of these electrodes using LTO revealed 350 cycles with good Coulombic efficiencies of more than 99 %. However, for full cells, only 35 cycles could be achieved during the cycling study.

In another approach, aluminium nano-rods were electrodeposited for implementation as a current collector in LIBs. The nano-structured deposits were obtained using a template. Electrodes were prepared with TiO₂ as an active material and 100 cycles could be achieved with very low capacities [6, 10, 11].

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Ultra thick electrodes, up to $\sim 80 \text{ mg cm}^{-2}$ mass loading, were prepared by Wang et al. using metal foam as a current collector. Bipolar cells were prepared to reduce the effective thickness of the electrodes and during the cycling study relatively good results could be achieved, when very low rates were applied (C/20, C/15 and C/5). They concluded that problems that have to be met with metal foam current collectors are cell shortening through damaging of the separator, and the difficulty of electrode calendaring (physical pressing), where the current collector could be destroyed [3, 12].

A 3D conductive network of ultrathin graphite foam as current collector was developed by Ji et al. The foam was prepared by precipitation of carbon at $1,050^\circ\text{C}$. Ni foam was exposed to CH_4 at high temperatures followed by removal of the Ni [13]. Due to the high temperatures, this procedure requires a lot of energy and the preparation of the current collector involves a disproportionate effort.

In our work, we developed a 3D current collector for the positive electrode based on a non-woven polyethylene terephthalate (PET) plated with aluminium by physical vapour deposition (PVD). The advantages of this new current collector are: reduced weight of inactive components, possibility of higher mass loadings without delamination of active material and reduced effort of metal, which is a critical point concerning sustainability. The advantages of our approach compared to the proposed methods in literature are an easy and economically feasible preparation, an excellent mechanical stability even during physical pressing (calendaring) of the electrode, excellent electrochemical cycling behaviour and rate capability of electrodes using this 3D current collector. Furthermore, this new 3D current collector has a smooth surface, and therefore, the problem concerning safety features through separator damaging is negligible [3].

2 Experimental

All electrochemical experiments were performed in a 3-electrode Swagelok[®]-T cell and metallic lithium served as a reference and counter electrode. Electrodes were prepared with following composition: 88 wt% LiCoO_2 (HC17 purchased from VARTA), 7 wt% Super-P Li (Timcal) as a conducting agent and 5 wt% polyvinylidenefluoride (Kynar 761) as a binder. The electrode slurry was prepared via a dispersing technique using N-methyl-2-pyrrolidone (Alfa Aesar, HPLC grade, 99.5 %) as a solvent. The slurry was coated both on a common flat Al foil (used as received) and on an Al-metallised 3D current collector (PET non-woven polymer). All electrodes were pre-dried at 333 K in air, and then subsequently dried at 353 K under vacuum (10^{-3} mbar) for 24 h. The average

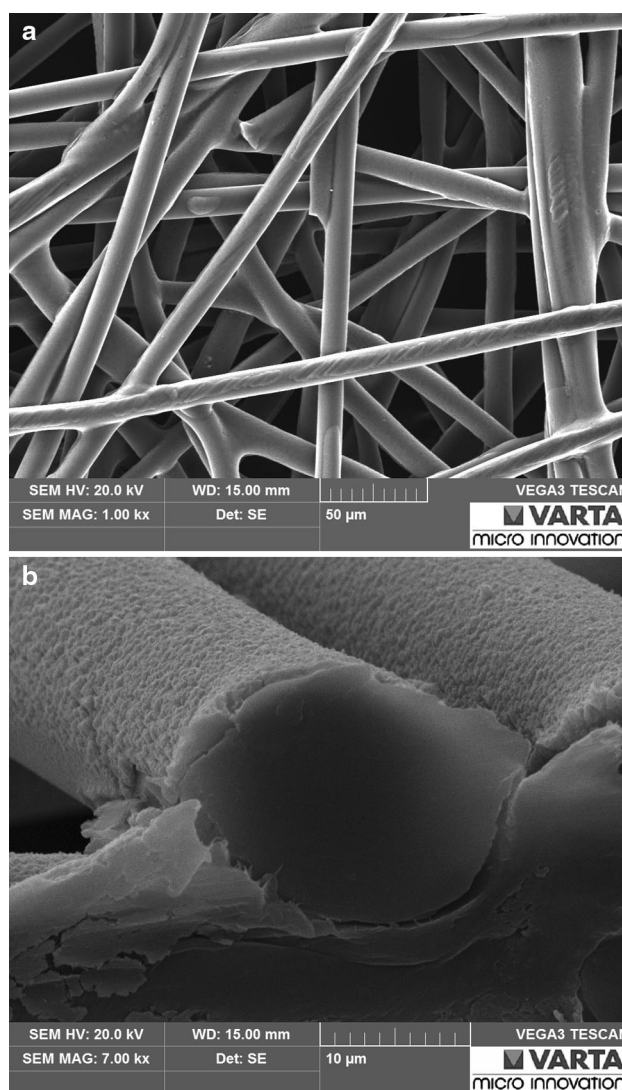


Fig. 1 SEM images of the surface **a** and cross section **b** of Al-plated non-woven PET

mass loading (m) of these electrodes was about $9\text{--}11 \text{ mg cm}^{-2}$.

Full cells were characterised in pouch bag configuration with electrode dimensions of $30 \times 50 \text{ mm}$ and a capacity of 2.1 mAh cm^{-2} . Cathode and anode were separated using a monolayer polypropylene membrane separator (Celgard[®] 2400). The electrolyte was composed of a mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) (EC/DEC 3:7 v/v) and 1 M LiPF_6 as a conducting salt. All test cells were assembled in an argon-filled glove box, in which the moisture and oxygen content were maintained below 0.1 ppm. The cyclic voltammetry experiments were performed with a potentiostat/galvanostat (Biologic VMP3) at a scan rate of $30 \mu\text{V s}^{-1}$ and the long-term cycling tests were performed with a MACCOR Series 4000 battery tester, both at 293 K. The half cells

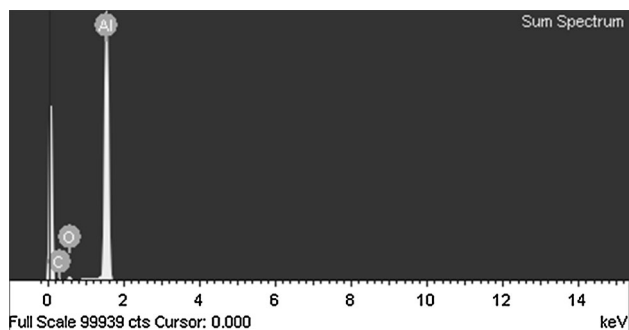


Fig. 2 EDX spectrum of Al-plated non-woven polymer

were cycled in the potential range between 3.5 and 4.2 V versus Li/Li^+ at a rate of 1.0 C and a period of constant voltage charge at 4.2 V for 1 h. The full cells were cycled in the potential range between 3.0 and 4.2 V versus Li/Li^+ at a rate of 0.1 C. For rate capability tests, the rate was gradually increased from 0.5 to 5.0 C.

In order to examine the operation voltage window of Al-plated non-woven polymer, half cells were fabricated, and the current collector was used as a working electrode. Lithium metal was used as a reference and counter electrode and a 1 M solution of LiPF_6 in ethylene carbonate (EC)/diethyl carbonate (DEC) (3:7 v/v) as electrolyte. To simulate a charging step over a long period of time and for proofing the electrochemical stability of the current collector, a constant voltage of 4.3 V versus Li/Li^+ was applied for a certain period of time and the resulting current was recorded.

Physical vapour deposition was carried out under reduced pressure using cathodic arc deposition, utilised with an Al target. Before deposition, the working piece was cleaned and activated in an argon/oxygen plasma.

Morphology analysis was performed using a Tescan Vega3 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray detector (Oxford Instruments INCAx-act) for determination of elemental composition of the deposits.

3 Results and discussion

A current collector with an Al layer thickness of 1 μm was prepared by PVD, and the resulting metal layer is relatively smooth, dense and homogenous as shown in Fig. 1. The EDX spectrum after aluminium deposition (Fig. 2) shows that a pure Al layer could be obtained. The detected oxygen could be attributed to passivation of Al on air during the transfer of the sample to the vacuum chamber of the SEM.

Figure 3 compares the cross section of an LCO-electrode with Al-plated non-woven polymer and Al foil as

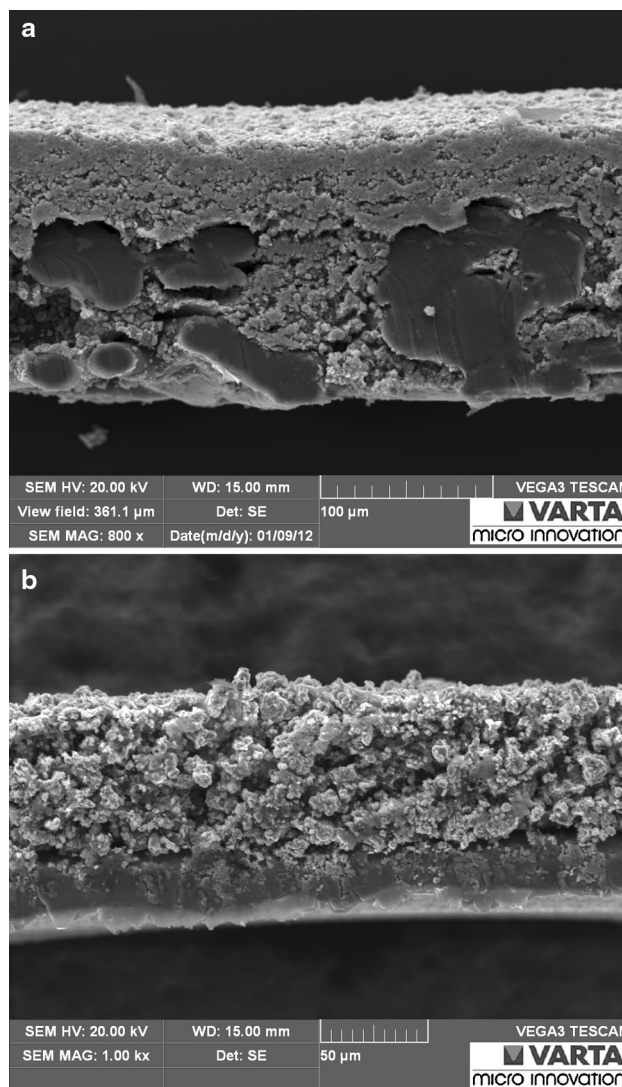
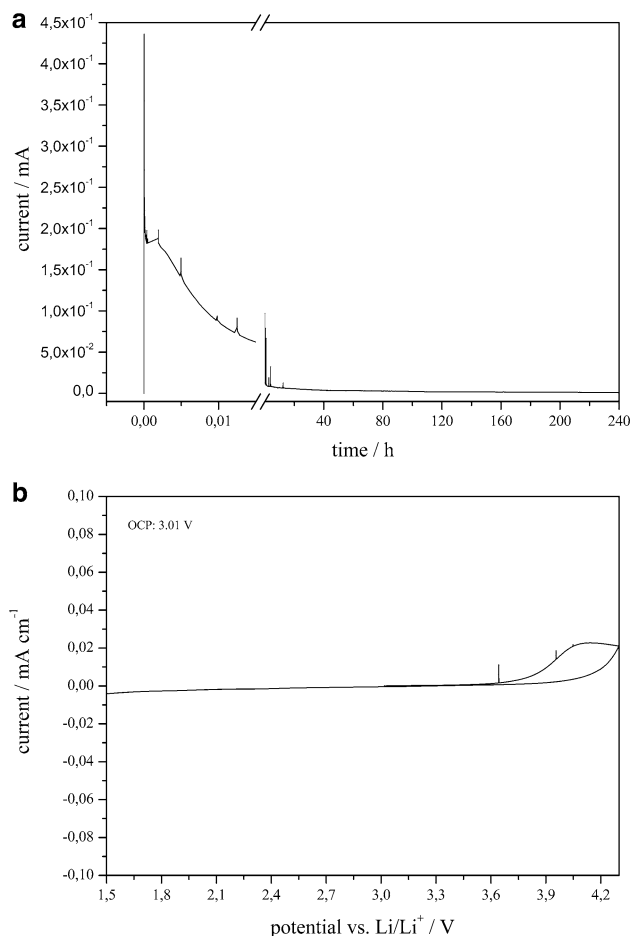


Fig. 3 SEM images of the cross section of LCO electrodes with a 3D current collector **a** Al foil as current collector **b**

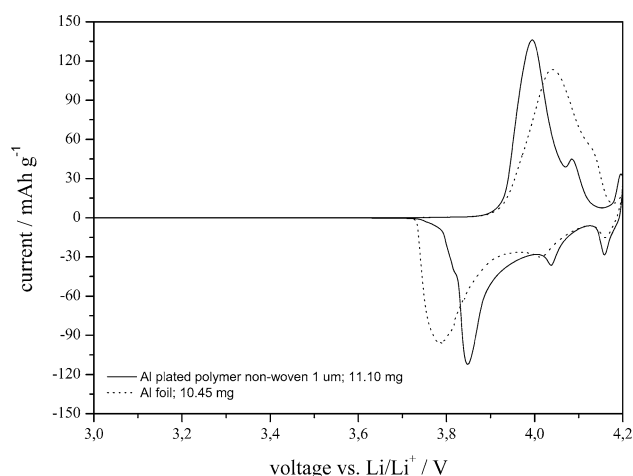
current collector. As shown in Fig. 3a, the active material fills the hollow space of the 3D current collector. These electrodes could be loaded with much higher masses of active material compared to electrodes with a flat metal substrate as current collector, without delamination of electrode material. The increased surface area leads to higher contact area of active material and current collector and will improve the mechanical stability of the final electrode with coating thicknesses up to 200 μm . Therefore, the application of higher current densities will be allowed. For comparison, thick LCO electrodes with Al foil as a current collector were fabricated and treated as electrodes with the 3D current collector. The coating with a thickness of 150 μm often delaminates from the 2D current collector and had bad final film morphologies.

Table 1 Comparison of mass, conductivity and thickness of two different current collectors

	Al foil	3D current collector
Mass [mg cm ⁻²]	7.54 ± 0.03	3.31 ± 0.09
Conductivity [S cm ⁻¹]	384,000 ± 21,000	49,000 ± 3,300
Thickness [μm]	33.07 ± 0.93	97.38 ± 2.29

**Fig. 4** Curve received from chronoamperometric measurement at a constant voltage of 4.3 V versus Li/Li⁺ for 200 h **a** and linear sweep voltammogram of the 3D current collector with a scan rate of 1 mV s⁻¹ **b**

Although the thickness of the 3D current collector is much larger compared to a typical Al foil (~100 μm versus ~30 μm), the average mass of the 3D Al-plated non-woven polymer is about 50 % less than that of Al foil (Table 1). Both the lower mass of the current collector and the possibility of higher mass loading will contribute to a higher specific energy on the final device.

**Fig. 5** Comparison of the second cycles of cyclic voltammetric measurement of electrodes with different current collectors; scan rate 30 μV s⁻¹

On the other hand, the conductivity of the metallised non-woven polymer is about 7–8 times lower compared to Al foil. Pure Al naturally forms a thin surface layer with a thickness of about 0.1–0.5 μm in contact with oxygen [14]. The higher the surface area, the more Al₂O₃ will be created on the surface of the working piece, and since Al₂O₃ is an insulating material, the conductivity will be reduced. Additionally, the template for the 3D current collector is an insulating material and will reduce the overall conductivity too. However, the complex geometry of the 3D current collector will affect the accuracy of calculation.

In order to examine the operation voltage window of Al-plated non-woven polymer, half cells were fabricated and the current collector was used as a working electrode.

As shown in Fig. 4a, the rapid decrease of the current at the beginning could be attributed to passivation effects of the Al current collector in the electrolyte solution [15, 16]. After this rapid decrease, the current flow is negligible. The linear sweep voltammogram (Fig. 4b) also proves the electrochemical stability of the 3D current collector in a potential range between 1.5 and 4.3 V versus Li/Li⁺. The small anodic peak observed at 4.0 V versus Li/Li⁺ can be attributed to passive film formation of the Al metal [2].

Therefore, metallised non-woven polymer was found to be electrochemically stable up to 4.3 V versus Li/Li⁺, and hence it could be established as 3D current collector for cathode materials like LCO or LiFePO₄. For electrochemical characterisation, LCO electrodes were fabricated and half cells were assembled as described before. The results for the cyclic voltammetry experiments of those electrodes are shown in Fig. 5.

Due to diverse mass loading of electrode material into the hollow spaces of the 3D current collector, determination of the exact mass and the C-rate is rather difficult. To

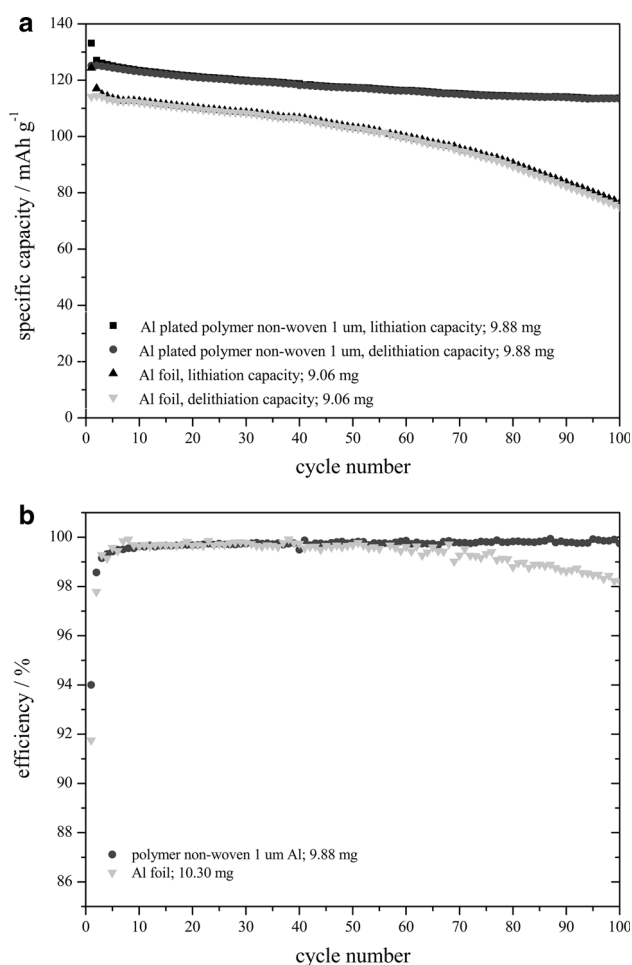


Fig. 6 Constant current cycling (c-rate: 1.0 C) of electrodes with non-woven polymer as 3D current collector, coated with 1 μm Al compared to Al foil as current collector **a** and accompanied efficiencies **b**

evaluate the C-rates, we calculated the 2nd lithiation capacities of the electrodes from the cyclic voltammetry experiments and used these values for the constant current cycling study (Fig. 6). The results show that the applied method for determination of the C-rate is highly suitable. Using the new 3D current collector, the theoretical capacity of half lithiation of LCO ($\sim 130 \text{ mAh g}^{-1}$) could be reached very well.

As can be seen in Fig. 6a, the electrodes with the 3D current collector could achieve a remaining capacity of 110 mAh g^{-1} after 100 cycles (1.0 C-rate), with a capacity loss of 17 % and an efficiency close to 100 %. In comparison, the capacity retention of the 2D current collector electrodes after 100 charge and discharge cycles is just 76 mAh g^{-1} , which means a capacity loss of 39 % (1.0 C-rate).

The efficiencies of the cycling study are shown in Fig. 6b. In consistence with the cycling study, the electrode with Al foil as a current collector exhibits a rapid decrease

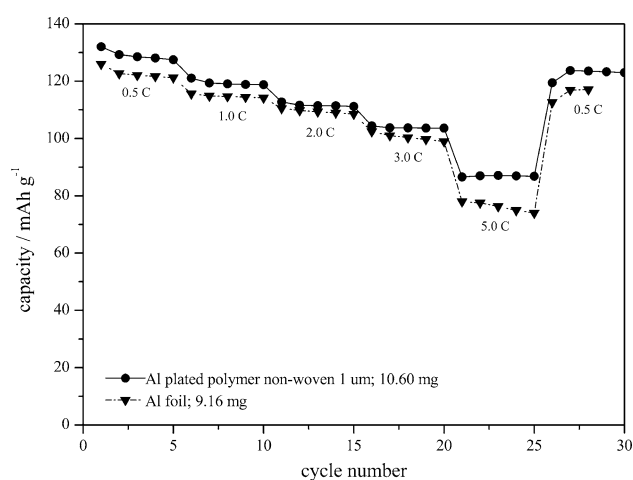


Fig. 7 Rate capability test of electrodes with non-woven polymer as 3D current collector, coated with 1 μm Al compared to Al foil as current collector

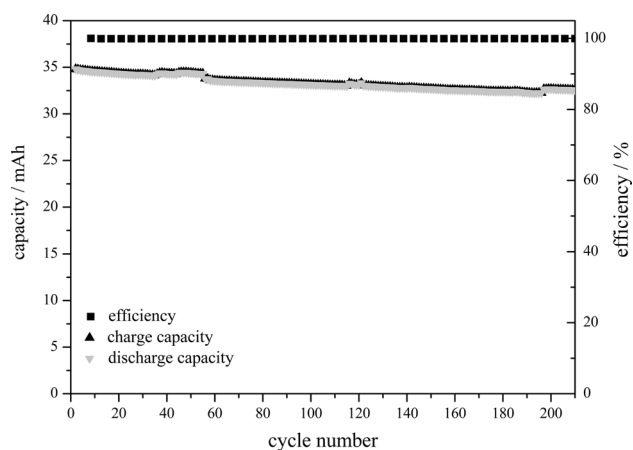


Fig. 8 Constant current cycling (c-rate: 0.1 C) of a full cell in pouch bag configuration using LCO with a 3D current collector as cathode and graphite coated on copper foil as anode

of efficiency from the 60th cycle, leading to tremendous capacity fade.

A rate capability test (Fig. 7) shows that the performance of the electrode with the metallised non-woven polymer is much better compared to conventional electrodes.

The new 3D current collector was also characterised in full cells (Fig. 8, constant current cycling study after one cycle formation). LCO, coated on Al-plated non-woven polymer was used as cathode and graphite coated on copper foil as anode. Fig. 8 depicts that the cycling characteristic of this cell reveals an excellent cycling stability.

It should be mentioned here that fabrication of all electrodes was carried out under lab conditions. These conditions are not favourable conditions for electrode preparation compared to industrial processes in terms of reproducibility.

We believe that the worse reversibility, performance, and the tremendous capacity fade of the electrodes with the 2D current collector could be on account of the poorer mechanical stability and higher resistivity. Due to flexibility of the 3D current collector, any volumetric changes of the electrodes during electrochemical reaction can be better accommodated, leading to improved rate capability and cycling stability.

4 Conclusion

In conclusion, we developed a novel type of flexible and lightweight 3D current collector for the positive electrode of LIBs to replace the commonly used flat metal foil. We embedded active material into the hollow architecture of a metallised non-woven polymer, leading to much better cycling performance with feasible higher mass loadings compared to conventional electrodes. In addition, the gravimetric energy density of a battery could be improved, when the heavier flat metal substrate is replaced by the novel 3D current collector. The metallised non-woven polymer contains 50 % less mass, and it can be used with a variety of electrode materials. The results of electrodes, composed of the new 3D current collector and LCO, showed excellent capacity retention and rate capability and can, therefore, be considered as appropriate alternative to “state of the art” Al metal foil current collectors. Furthermore, we revealed an easy and economically feasible production way for 3D current collectors with outstanding mechanical stability compared to 3D current collectors delineated in literature. PVD of Al has been scaled up already to meet industrial requirements [17], and thus mass production of lightweight and flexible current collectors for the cathode of LIBs is potentially feasible. Because of its excellent mechanical stability, electrodes with this flexible non-woven polymer could be calendered without damaging the current collector, which is in turn an important feature for electrode production in battery manufacturing. Moreover, this new 3D current collector has a smooth surface, and therefore, the problem concerning safety features through separator damaging is negligible.

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